142. *The Thickness of Air-formed Oxide Films on Iron.*

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Estimates of the thickness of air-formed oxide films on high-purity iron and on mild steel have been derived from the chemical analysis of films stripped from the underlying metal by treatment in a solution of iodine in anhydrous methyl alcohol, in absence of air. The data, supplemented in certain cases by determination of total oxygen in the surface film by Sloman's vacuum-fusion method, have been correlated with gravimetric determinations of oxygen taken up during exposure to air. Specimens prepared by abrasion carried, before the initial weighing, 1·5 μg. of oxygen per sq. cm. of apparent area. It was concluded that this was present as discontinuous ferric oxide in a matrix of iron, the total thickness of heterogeneous material being 140 A. (calculated on the apparent area of specimen) or 56 A. (on the estimated "real" area). Films stripped from specimens heated to the first-order blue (275°) incorporated this primary oxide, but from specimens heated to the first-order straw-colour (225°) only oxide formed during the period of heating was removed. The following values were obtained for total thickness of material—including continuous "secondary" film and heterogeneous primary layer beneath. First-order straw: 350 A. (apparent area), 140 A. (estimated real area). First-order blue: 590 A. (apparent area), 240 A. (estimated real area).

ESTIMATES of the thickness of very thin oxide films on iron were first attempted by optical methods [discussed by Evans, "Metallic Corrosion, Passivity and Protection" (Arnold), Appendix], *e.g.*, the simple comparison of colours produced on heating against "Newton's ring" colours for air (interference phenomena being assumed in the oxide film) as used by

Tammann *et al.* (*Z. anorg. Chem.*, 1920, **111**, 78 *et seq.*), and the spectrophotometric method of Constable (*Proc. Roy. Soc.*, 1927—1928, *A*, **117**, 376, 386). Other considerations apart, such methods are limited in their application, since the characteristic colours are produced on polycrystalline surfaces only at temperatures exceeding 200° (Vernon, *Trans. Faraday Soc.*, 1935, **31**, 1668). Evans and Stockdale (J., 1929, 2651) carried out a few determinations by estimating the ferric iron content of films stripped anodically from heat-treated iron. From the increase in weight due to oxidation, Vernon (*loc. cit.*) deduced corresponding thicknesses for films in both the " visible " and the " invisible " range. Miley (*Carnegie Schol. Mem.*, 1936, **25**, 197; see also discussion, *J. Iron Steel Inst.*, 1937, **135**, 407P), in an intensive investigation, measured the millicoulombs of electricity required to reduce the film after exposure to air at several temperatures; he concluded that the marked discrepancies between thickness values obtained by optical and gravimetric methods were due to the presence on abraded specimens of an initial oxide film, of which the subsequent weight-increments took no account. Miley suggested that confusion had arisen because different meanings had been ascribed to the term " thickness," and in his own work he defined thickness as " the mean general intercept " or the mean of the intercepts made by the film on lines normal to the *general* plane of the surface. This intercept would be identical with the *local* thickness of the film only on a surface the irregularities of which were negligible compared with film thickness. For surfaces mechanically prepared by turning or abrading with emery (such as those used by the present authors) this condition does not hold, but since the real surface area is not known, Miley's definition is useful so long as it is remembered that the term " thickness " is used in an artificial sense. For purposes of comparison it is probably still more convenient to express results simply as weight of oxygen (as oxide) per sq. cm. of apparent area, and this method is followed in the present work.

From his electrometric method Miley obtained film-thickness values which agreed well with those determined optically by Constable (*loc. cit.*). He concluded that the thickness of the primary oxide film (assumed to be Fe_2O_3) on an iron surface after abrasion with fine emery (followed by one day's exposure to dry air at 25°) was 210 A. (3·3 μg. of oxygen/cm.^{2}), which, if Erbacher's (*Z. physikal. Chem.*, 1933, **163**, 215) estimate of $2\frac{1}{2}$ is adopted for the ratio of real to apparent area, corresponds to a film thickness of the order of 80 A., if calculated on the real area. Miley believed that this was identical with the " homogeneous " or outer surface layer of Evans and Stockdale (*loc. cit.*); as these authors had postulated a zone below this surface layer consisting of a mixture of " shattered " metal and oxide (the " mixed zone "), it is clear that Miley's value corresponds to a still greater thickness of *total oxide*. Special importance has been attached by Miley and others to the agreement of results obtained by any given method of film-thickness estimation with Constable's optically-derived values. This criterion would seem, however, to be of doubtful validity, inasmuch as the optical method involves in its application a number of assumptions—notably that the thin transparent film in intimate association with the metal has both the same composition and the same optical properties (particularly refractive index) as massive ferric oxide; it also assumes that at the lower reflecting surface there is an abrupt transition from a layer with optical properties of the oxide to one having the optical properties of the metal.

As the thickness of the primary oxide film is considered to have an important bearing on some of the more fundamental aspects of both atmospheric and immersed corrosion, the present work was undertaken with the object of throwing further light on this question.

EXPERIMENTAL.

The procedure in the main experiments consisted in the chemical analysis of films stripped from specimens after exposure to air at various temperatures (ferric and ferrous iron directly, oxygen by calculation), the oxygen taken up during exposure being determined by the increase in weight of the specimen. For these experiments, mild-steel sheet (thickness, 0·75 mm.; analysis: C, 0·08; Si, 0·01; Mn, 0·39; S, 0·04; P, 0·035; Cu, 0·10%) was used as in previous work on the oxidation of iron (Vernon, *loc. cit.*). Similar methods of surface preparation (Hubert No. 1 emery paper finally), degreasing, heat-treatment, and of weighing were also employed. Weight-increments were determined normally on specimens measuring 5 × 5 cm. from which specimens for stripping (approximately 5 × 2 cm.) were cut. Following Evans (J., 1927, 1024; *Nature*, 1927, **120**, 584), in order to ensure freshly-cut edges, this was done immediately before immersion in the stripping solution (see below), the precise dimensions being determined for each specimen after cutting. An invaluable supplementary method, applicable, however, only on a limited scale and only on specimens of high-purity iron, has been rendered available through the co-operation of Mr. H. A. Sloman, of the Metallurgy Department, National Physical Laboratory, *viz.*, the determination of the total oxygen content of suitable specimens (before and after exposure or before and after abrasion) by the vacuum-fusion process (Iron and Steel Institute, Seventh Report on Heterogeneity of Steel Ingots, First Oxygen Sub-committee Report, 1937, 82), the application of which to the present work is discussed later (see also Appendix).

The method of stripping was developed from the original chemical method of Evans (*loc. cit.*, 1927), in which the oxide film was undermined and dislodged from the specimen by immersion in a saturated solution of iodine in a 10% aqueous solution of potassium iodide (followed usually by washing the film with dilute hydrochloric acid to remove ferric hydroxide formed during the stripping process). In the technique he has recently described (Iron and Steel Institute, Fifth Report of Corrosion Committee, 1938, 225) for the transfer of thin oxide films from metal to celluloid, Evans uses a modified form of his anodic stripping method (*loc. cit.*, 1927; Evans and Stockdale, *loc. cit.*). For the purpose of the present work the authors have preferred the use of iodine; they have, however, sought to refine the method in such a way that the oxide film might be removed quantitatively without risk of augmentation during the stripping process.

A large number of preliminary experiments, both qualitative and quantitative, with the aqueous iodine reagent showed that in the presence of traces of dissolved oxygen any initial oxide dislodged during treatment is reinforced by a film (probably of hydroxide) precipitated from solution. Thus, the thickness of the film stripped from specimens exposed to purified air at 25° for periods varying from 1 minute to 7 days was found, within experimental error, to be independent of period of exposure, although the thickness of the primary film is known to increase measurably during that period; the precise value actually exceeded that obtained, by the improved method to be described, from specimens carrying the blue interference-colour film produced at 275°. Moreover, the thickness of the stripped film increased with the volume of iodine solution employed, although the characteristic appearance of the film, showing the scratch-lines of the original abraded surface, was not appreciably altered. Confirmation that the augmentation of film thickness was due to precipitation was obtained by the stripping of a further (" spurious ") film on returning to the solution, without delay, a specimen from which the primary film had already been stripped.

By using an apparatus in which the stripping operation could be conducted with an atmosphere of nitrogen or argon over the reagent, it was found that for any given initial film the more thoroughly oxygen was excluded from the system the smaller became the value obtained for film thickness. It was concluded that " contamination " of stripped films is due, in general, to (i) obviously precipitated ferric hydroxide, readily distinguishable by its colour, due to the presence of grosser amounts of oxygen in the aqueous solution, (ii) transparent, colourless oxides that are indistinguishable from, and add to the continuity and thickness of, any film initially present on the metal. It became evident that for the elimination of the second type of contamination complete exclusion of both oxygen and water was necessary; this was rendered possible by the use of the reagent employed by Rooney and Stapleton (*J. Iron Steel Inst.*, 1935, **131**, 249) for the estimation of oxide inclusions in steel, *viz.*, a solution of iodine in anhydrous methyl alcohol. This reagent is capable of dissolving iron completely, without any attack even on finely disseminated iron oxide; as in the case of the aqueous solution, however, it was unnecessary to dissolve the whole of the underlying iron, since attack by the iodine occurs preferentially just below, with consequent loosening of, the film.

The method finally adopted is carried out as follows: Anhydrous methyl alcohol (a commercial synthetic product) is refluxed with and distilled from quicklime, and redistilled from calcium metal. " AnalaR " iodine is dried over silica gel in a desiccator for several days, 7 g. (sometimes 3·5 g. for very thin films) are dissolved in 60 ml. of the dry alcohol, and the solution filtered through Whatman No. 50 filter-paper into flask *A* (Fig. 1). Flask *B* contains about 150 ml. of the dry alcohol. After a preliminary passage of nitrogen, the specimen *S* is hung on the glass hook carried in the rubber bung of the reaction tube *R*, which is then thoroughly swept out with dry oxygen-free nitrogen (commercially "oxygen-free," passed over heated copper and phosphoric oxide). This is effected by opening the taps *T* and *V* (clips *a* and *b* being open, *c* and *d* closed, and tap *W* open to the exit *D*). Air is removed from flask *A* by closing *b* and opening *d*, *e*, and *g* (*U* being open to *D*), the iodine solution being boiled and cooled three times whilst nitrogen is passing through. A similar procedure is employed to de-aerate the alcohol in *B*, *f* and *h* being open. The iodine solution is then forced into the tube *R* (*T* opened to *U*; *g*, *e*, *d*, *b* open, *W* open to exit *D*) so that the specimen *S* is completely immersed. *W* and *b* being closed, the specimen is left until " undermining " is completed (30—90 mins.); the film is then characteristically " wrinkled," although still clinging to the metal, and the iodine solution is largely decolorised. After the liquid has been carefully run out by opening *b* and *c*, alcohol is slowly forced into *R* by opening *h*, *f*, and *d*, the process being repeated several times until all excess iodine has been washed into *C*. The specimen is then carefully transferred to a dish of dry methyl alcohol, in which, on gentle shaking, the film becomes completely detached, breaking into fragments which usually curl into " rolls " (cf. Evans, *loc. cit.*, 1927) as it leaves the specimen. All the films that have been produced in this way are transparent (pale brown by transmitted light); they exhibit bright metallic reflection and clearly show the original scratch-lines of the metal. Under the microscope they appear clean and free from particles of metal or other spots of contamination. Photographs of typical specimens are shown as follows:

FIG. 1.

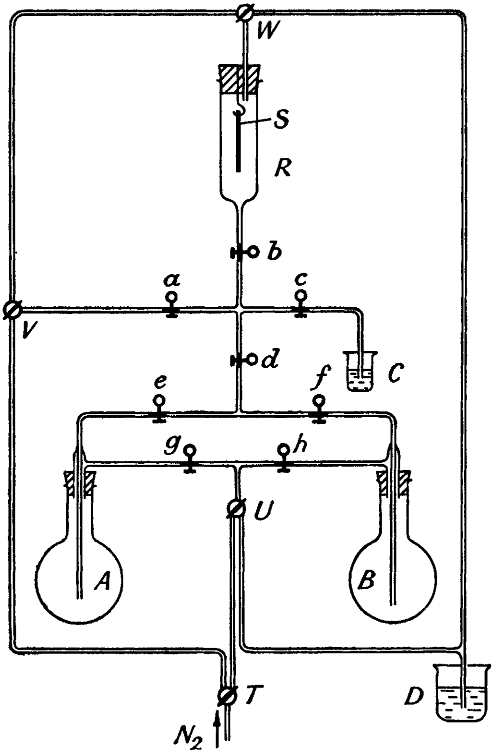


Fig. 2. " Uncontaminated " film stripped from blue heat-tinted iron by standard method (this film happened to leave the specimen before removal from the reaction tube, and is photographed through the walls of the tube, to which it is still adhering).

Fig. 3. Portion of film similar to above, × 50.

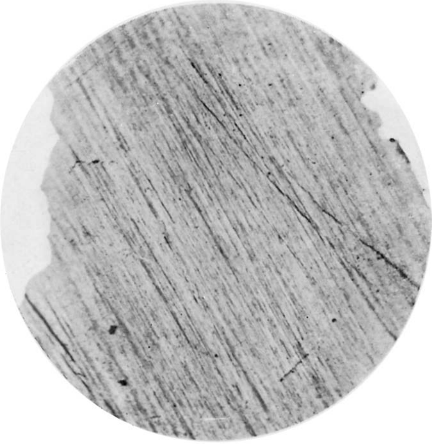
Fig. 4. Portion of " contaminated " (" augmented ") film (× 50) stripped from " straw " heat-tinted iron in the aqueous reagent (*supra*). As in Fig. 3, the original (in this case intersecting) scratch-marks are clearly visible.

Fig. 5. Portion of " spurious " film (× 50) obtained by leaving in the aqueous reagent (in contact with air) a specimen from which an augmented air-formed film had already been stripped. Naturally, this specimen does not show scratch-marks.

FIG. 2.

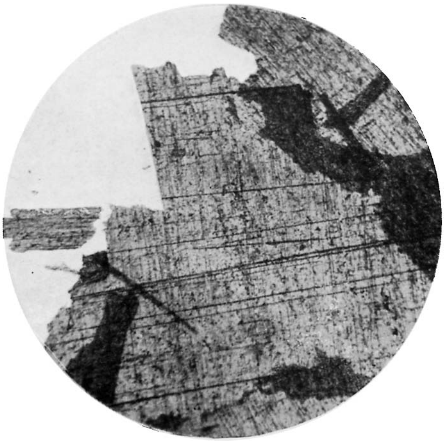
Stripped film (from blue heat-tinted iron) in reaction tube. (Legend beneath shows transparency of film, except where folded.) (× 1½.)

FIG. 3.



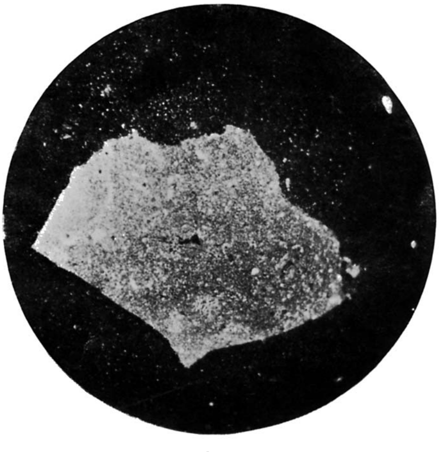
Portion of film (supra). (×50.)

FIG. 4.



Portion of "contaminated" film. (× 50.)

FIG. 5.



Portion of "spurious" film (see p. 624). (× 50.)

[*To face p.* 624.

For the purpose of analysis, the fragments of film obtained by the standard method are transferred immediately from the dish of methyl alcohol to a sintered-glass filter. In separating films from mild steel an appreciable amount of dark magnetic material settles to the bottom of the dish. Under the microscope this appears as bright metallic-looking particles, and chemical analysis reveals a considerable iron content. As no such material separates when pure iron is treated, it probably consists of iron carbide which has escaped attack by the iodine. In carrying out a determination, this magnetic material is retained by means of a magnet underneath the dish, the film fragments being then readily washed on to the filter without contamination. They are washed repeatedly with dry methyl alcohol, followed by boiling distilled water, and then immediately dissolved in 20 ml. of hot 50% hydrochloric acid (" AnalaR ") and the solution made up to 100 ml., 10 ml. of which are taken for each colorimetric determination. Ferric iron is estimated by the thiocyanate method against a standard iron solution containing the same concentration of acid as the sample, ferrous iron by 2 : 2′-dipyridyl, a standard containing the same amount of ferric iron as the sample being used. (Results agreed, within 10 μg., with determinations of total iron by both methods.)

TABLES I—XIII.

Oxygen Contents of Films (μg./cm.^{2}).

(" Oxygen equivalent of $\mathrm{Fe}^{\cdots}$ " and " Oxygen equivalent of total Fe " refer throughout to values obtained by chemical examination of the *stripped* films.)

I. *Mild steel : first-order straw film* (150 mins. at 225°).

						Mean.
From weight-increment	2·9	3·0	2·7	2·7	2·8	2·8
Oxygen equivalent of $\mathrm{Fe}^{\cdots}$	3·2	3·3	3·2	3·2	2·9	3·2
Oxygen equivalent of total Fe	3·5	3·6	4·2	4·2	3·2	3·7

II. *Mild steel : first-order blue film* (75 mins. at 275°).

									Mean.
From weight-increment	6·4	6·4	6·4	6·4	6·4	6·6	6·6	6·5	6·5
Oxygen equivalent of $\mathrm{Fe}^{\cdots}$	8·5	7·3	7·1	8·7	7·1	6·5	7·2	7·2	7·5
Oxygen equivalent of total Fe	9·6	8·4	9·0	11·0	9·8	9·1	9·4	9·2	9·4

III. *Pure iron : " primary film "* (abrasion + 1 hour at 25°).

			Mean.
From vacuum fusion	1·5	1·5	1·5
Oxygen equivalent of $\mathrm{Fe}^{\cdots}$	0·6	0·5	0·6
Oxygen equivalent of total Fe	0·6	0·5	0·6

IV. *Mild steel : " primary film "* (abrasion + 1 hour at 25°).

							Mean.
Oxygen equivalent of $\mathrm{Fe}^{\cdots}$	0·5	0·6	0·3	0·2	0·3	0·7	0·4
Oxygen equivalent of total Fe	0·5	0·6	0·5	0·2	0·4	0·9	0·5

V. *Mild steel : " thickened primary film "* (8 days at 25°).

			Mean.
From weight-increment	0·4	0·4	0·4
Oxygen equivalent of $\mathrm{Fe}^{\cdots}$	0·6	0·6	0·6
Oxygen equivalent of total Fe	0·8	0·9	0·9

VI. *Pure iron : first-order straw film* (96 mins. at 225°)

					Mean.
From weight-increment (*W.I.*)	3·2	3·1	2·7	2·7	2·9
From vacuum fusion (primary film) + *W.I.*	4·7	4·6	4·2	4·2	4·4
Oxygen equivalent of $\mathrm{Fe}^{\cdots}$	3·2	3·1	2·7	2·9	3·0
Oxygen equivalent of total Fe	3·4	3·2	3·0	3·2	3·2

VII. *Pure iron : first-order blue film* (50 mins. at 275°).

					Mean.
From weight-increment (*W.I.*)	7·2	6·8	6·9	6·8	6·9
From vacuum fusion (primary film) + *W.I.*	8·7	8·3	8·4	8·3	8·4
Oxygen equivalent of $\mathrm{Fe}^{\cdots}$	7·6	8·5	7·2	8·4	7·9
Oxygen equivalent of total Fe	9·0	9·9	9·0	9·3	9·3

VIII. *Mild steel: first order straw film* (14 mins. at 275°).

			Mean.
From weight-increment	2·8	2·8	2·8
Oxygen equivalent of Fe$^{\cdot\cdot\cdot}$	3·0	3·0	3·0
Oxygen equivalent of total Fe	4·5	4·6	4·6

IX. *Mild steel: first-order blue film* (17 hrs. at 225°).

				Mean.
From weight-increment	6·4	6·4	6·4	6·4
Oxygen equivalent of Fe$^{\cdot\cdot\cdot}$	6·3	5·5	5·6	5·8
Oxygen equivalent of total Fe	7·8	7·4	7·1	7·4

X. *Pure iron: "advanced" first-order blue film* (75 mins. at 275°).

					Mean.
From weight-increment (*W.I.*)	7·1	9·4	8·9	9·2	8·6
From vacuum fusion (primary film) + *W.I.*	8·6	10·9	10·4	10·7	10·1
From vacuum fusion (total film)	10·2	10·3			10·3
Oxygen equivalent of Fe$^{\cdot\cdot\cdot}$	11·3	12·0	12·6	11·5	11·8
Oxygen equivalent of total Fe	13·4	13·3	14·4	13·2	13·6

XI. *Mild steel (pre-exposed at 25° for 1262 days): straw film* (96 mins. at 225°).

			Mean.
From weight-increment at 25°	12·0	12·0	12·0
From weight-increment at 225°	2·0	2·0	2·0
Oxygen equivalent of Fe$^{\cdot\cdot\cdot}$	2·8	2·5	2·6
Oxygen equivalent of total Fe	3·4	3·1	3·2

XII. *Mild steel (pre-exposed at 25° for 1262 days): mauve film* (50 mins. at 275°).

			Mean.
From weight-increment at 25°	11·6	11·6	11·6
From weight-increment at 275°	4·3	4·3	4·3
Oxygen equivalent of Fe$^{\cdot\cdot\cdot}$	7·3	7·3	7·3
Oxygen equivalent of total Fe	8·3	8·0	8·1

XIII. *Mild steel (pre-exposed at 25° for 1262 days): no subsequent heat-treatment.*

			Mean.
From weight-increment	11·6	11·6	11·6
Oxygen equivalent of Fe$^{\cdot\cdot\cdot}$	0·8	1·2	1·0
Oxygen equivalent of total Fe	1·1	1·6	1·3

RESULTS AND DISCUSSION.

The data necessary for the computation of film thickness are set out in Tables I—XIII in the form of oxygen contents; these are derived, in the main, from the weight-increments of the specimen after exposure, and from oxygen equivalent both to ferric iron and to total iron in the film. Ferric iron found by analysis is assumed to represent ferric oxide * in the film before stripping. Although the total iron has frequently exceeded ferric iron, it cannot be assumed that the difference is due to ferrous oxide in the film, since metallic iron would be similarly reported.

Results obtained (Tables I and II) for the first-order straw film (225°) and for the first-order blue (275°) show that the difference between total and ferric iron is appreciably greater for the blue than for the straw film. In the case of the latter film no distinction can be made, within experimental error, between values given by weight-increment and by the ferric iron content after stripping; the blue film, however, has given appreciably greater values by the stripping method ("ferric oxygen") than by weight-increment. On the assumption that the abraded surface of the specimen carries a certain amount of oxide when the initial weighing is made (p. 622), these results indicate that the blue film,

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* Preston and Bircumshaw (*Trans. Faraday Soc.*, 1935, **31**, 1677), from electron-diffraction examination of abraded iron surfaces after heating in air, concluded that the surface film consisted of α-ferric oxide above 200° and either γ-ferric oxide or magnetite below (*ca.*) 200°. Nelson (*J. Chem. Physics*, 1937, **5**, 252; 1938, **6**, 606), also by electron diffraction, found the α-pattern at temperatures as low as 130° provided sufficient time was allowed; at and above 193°, however, the first-order blue interference colour was characterised by a new and more coarsely crystalline α-Fe_2O_3 having a different type of preferred orientation. At lower temperatures than the above, "mixed patterns" (showing the presence of metallic iron together with oxide) were observed in the early stages of exposure.

when stripped from the metal, incorporates at least some of the primary oxide,* whereas none of this is included in the detached straw film.

The " vacuum-fusion method " as developed by Sloman (*loc. cit.*) offered a means of determining with precision the amount of oxide in the freshly-abraded surface, provided the necessary area/weight ratio could be realised. As this was possible only for highly pure iron, a new series of experiments was carried out with material of the highest purity, prepared in the Metallurgy Department of the National Physical Laboratory. Satisfactory agreement between the vacuum-fusion tests and gravimetric results, under conditions within which they are directly comparable, was first established, as shown in Table X (also Appendix, p. 631) to which reference will be made later. In the authors' view the former method affords, where applicable, the most satisfactory and unequivocal basis for estimating the total amount of oxygen in surface films; in the present work it has been used as the criterion against which results obtained more conveniently by other methods have been checked.

The determination of oxygen introduced into the surface as oxide during abrasion, together with any formed by an hour's subsequent exposure to air (a period approximately equal to that which normally occurs between abrasion and weighing), is described in the Appendix; the value given by closely agreeing duplicate experiments was 1·5 μg./cm.^{2}. These experiments were conducted on the high-purity iron; attempts to obtain comparable values both on the pure iron and on the mild steel by the stripping-analysis method yielded results shown in Tables III and IV. The agreement between these values strongly suggests that the primary oxide behaves similarly both on pure iron and on mild steel. In the case of pure iron, however, the vacuum-fusion value is nearly 3 times that given by stripping, indicating that only a portion of the primary oxide is capable of removal in this way. The absence (within experimental error) of ferrous iron in each case will be noted.

Results obtained from the stripping of the film formed on mild steel after 8 days' exposure to purified air of 10% relative humidity at 25° (the " thickened primary film ") are shown in Table V. On the assumption that the amount of primary oxide on mild steel is similar to that on pure iron, the results of Table V confirm those of Table III in that a portion only of the primary oxide, after being augmented by exposure at 25°, is removable by stripping.

Values for coloured films on pure iron, corresponding with those of Tables I and II for mild steel, are shown in Tables VI and VII. It is remarkable that to produce a given change in colour shorter periods of exposure at the same temperature are required for pure iron than for mild steel, notwithstanding that the corresponding weight-increments are the same. The reason for this is not fully understood, although supplementary experiments have shown that the 0·1% of copper present in the steel is at least partly responsible. As in the case of mild steel, the ferrous iron content of the stripped film is greater for the blue than for the straw, whilst ferric iron again agrees with that given by weight-increment for the straw and exceeds that value for the blue film. Now, however, the sum of the values given by vacuum-fusion and weight-increment (which must include the whole of the oxygen present in the surface, including both the superficial continuous oxide and any " mixed zone " below) exceeds the " ferric oxygen " in the stripped straw film but shows approximate agreement with the " ferric oxygen " in the blue film. It follows, therefore, that the stripping operation removes the whole of the surface oxide constituting the blue film but only a portion of this oxide (the portion corresponding to weight-increment) in the case of the straw film (cf. results for mild steel, p. 626).

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* " Primary oxide " here refers to any oxide incorporated in the surface during the initial preparation of the specimen, together with any formed by simple contact with air during the first hour, this being the earliest time from which quantitative data are available for rate of oxidation (Vernon, *loc. cit.*). The term " primary oxide film " has been used by Vernon (*loc. cit.*) and Nelson (*loc. cit.*) to denote any invisible film formed during the early stages of exposure at ordinary temperatures (cf. " air-formed film " of Evans), but in the light of the present results it is doubtful whether the word " film," in the sense of a *continuous* entity, is correctly applied in this connection. The term " secondary film " (or " weight-increment film ") is used in the text to denote the film formed, by heating or otherwise, subsequent to the initial weighing of the specimen.

In order to decide whether this phenomenon is a function simply of the thickness of the respective films, or whether it is determined by temperature, experiments were carried out with the thinner (straw) film produced at the higher temperature (Table VIII) and the thicker (blue) film produced at the lower temperature (Table IX). In each case only the " weight-increment portion " of the film was removed; hence, film thickness alone cannot control the " incorporation " of primary oxide, since this takes place only at the higher temperature and then only provided that sufficient time be allowed. On the other hand, the reproduction of a given colour is determined by the thickness of the secondary film, and is unaffected by the incorporation or otherwise of the underlying primary oxide. The penetration of iron into the film at constant temperature (this being assumed to be responsible for the excess of total over ferric iron) appears to be favoured by time (cf. Tables I and IX, 225°; VIII and II, VII and X, 275°).

Table X shows the results obtained by heating pure iron at 275° for the same time as the mild steel in Table II (as already noted, this gives a more advanced blue, with corresponding greater weight-increment). This table includes vacuum-fusion values for the *total surface oxygen* after heat-treatment; these show satisfactory agreement with the values obtained by adding to the " weight-increment oxygen " the oxygen found by vacuum-fusion in the primary film. The oxygen equivalent to $Fe^{\cdots}$ as found by analysis, although slightly in excess,* confirms the foregoing conclusion that the stripped film includes the whole of the primary oxide under these conditions.

The influence of much thicker (invisible) films formed at low temperatures by the thickening of the primary film (cf. Table V) was further investigated by using specimens that had been exposed for 1262 days at 25° to purified air of 10% relative humidity, giving weight-increments equivalent approximately to an oxygen content of 12 μg./cm.^{2}. Two of the specimens were heated in air for 96 mins. at 225° (Table XI) whereby a straw-coloured film was obtained, and two for 50 mins. at 275° (Table XII) with the production of a mauve film, intermediate in the usual colour sequence between straw and blue. Notwithstanding the relatively heavy films carried initially, these colours and also the weight-increments on heating were much the same as those produced on heating freshly-abraded specimens at the same temperatures and for the same times, except that the colours were not quite so uniform or pure. These results suggest that the films responsible for the colours are formed *outside the film produced at* 25°. Attempts to isolate this long-period film resulted (Table XIII) in the isolation of only a small fraction of the film.

However, the difference between the value so obtained (" ferric oxygen " figure) and the corresponding value for the film stripped after heating at 225° (Table XI) shows close agreement with the weight-increment, *viz.*, 2·0 μg./cm.^{2}. On the other hand, the difference in the case of the film produced at 275° (Table XII) is greater than the corresponding weight-increment, confirming the conclusion already reached that the higher temperature favours the incorporation of primary oxide into the film removed by stripping. The remarkable result now emerges, however, that the maximum amount so incorporated is not greatly affected even when the thickness of the primary film has been increased many times by long pre-exposure to air. This is shown by the close agreement in the appropriate data for freshly-abraded (Tables I and II) and pre-exposed specimens (Tables XI and XII).

The complete data (mean values from Tables I—XIII) are summarised in Table XIV.

Conclusions.—The foregoing results may be used to estimate (1) the thickness of the " primary film," produced by abrasion followed by one hour's exposure to purified air at 25°; (2) the thickness of the " temper-colour film " formed as the result of exposure to air at the appropriate temperature.

(1) Although the vacuum-fusion results give accurately the total amount of oxygen in the surface film, its distribution is largely a matter of conjecture. On the basis adopted by Miley (*loc. cit.*), *i.e.*, assuming a uniform and homogeneous film of ferric oxide and a surface area equivalent to the nominal or apparent area, the oxygen content of 1·5 μg./cm.^{2} corresponds to a thickness of 95 A. (or 40 A. according to Erbacher's estimate of real area). This value includes the whole of the surface oxygen (cf. Miley's value of 210 A., which

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* The slight excess of ferric iron found in some of the experiments may be due to oxidation of ferrous iron during the separation and dissolution of the film.

TABLE XIV.

Summary of Results : Oxygen Contents of Films (μg. per sq. cm.).

	Films formed at ordinary temperature.				Films formed on heating.								
	" Invisible."				Straw colour.				Blue colour.				
	Iron.	Mild steel.			Iron.	Mild steel.			Iron.		Mild steel.		
Values obtained by	1 hr.	1 hr.	8 days.	1260 days.	225°. 96 mins.	225°. 150 mins.	275°. 14 mins.	225°. 96 mins.	275°. 50 mins.	275°. 75 mins.	275°. 75 mins.	225°. 17 hrs.	275°. 50 mins.
Weight-increment	—	—	0·4	11·6	2·9	2·8	2·8	2·0*	6·9	8·6†	6·5	6·4	4·3*
Vacuum-fusion	1·5	—	—	—	—	—	—	—	—	10·3	—	—	—
Vacuum-fusion (primary film) + weight-increment	—	—	(1·9)‡	(13·1)	4·4	(4·3)	(4·3)	—	8·4	10·1	(8·0)	(7·9)	—
Oxygen equivalent to $Fe^{\cdot\cdot\cdot}$ in stripped film	0·6	0·4	0·6	1·0	3·0	3·2	3·0	2·6	7·9	11·8	7·5	5·8	7·3
Oxygen equivalent to total Fe in stripped film	0·6	0·5	0·9	1·3	3·2	3·7	4·6	3·2	9·3	13·6	9·4	7·4	8·1
Details in table...........	III	IV	V	XIII	VI	I	VIII	XI	VII	X	II	IX	XII

* Values obtained by heat-tinting specimens *after long pre-exposure to air* at " ordinary temperature " (col. 13)

† " Advanced " blue colour.

‡ Values in parentheses (mild steel) assume same amount of oxygen in primary film as obtained by vacuum-fusion for iron.

included only the " homogeneous " surface layer and excluded the " mixed zone " presumed to lie beneath) but clearly it represents the lower limit of possible film thickness. The upper limit is derived by assuming that the content of oxygen is distributed in such a way that there is a gradual transition from ferric oxide at the outer surface to iron at a lower, ill-defined interface, where the oxide-carrying layer merges into unoxidised metal. On this basis, a thickness of 140 A. is obtained (" nominal area " is assumed in this and the following examples). A further alternative, which, on physical grounds, appears to be the most probable, assumes that " granules " of ferric oxide are incorporated sporadically in a matrix of iron. The thickness corresponding to this distribution is not likely to differ materially from the second derived value (140 A.), but this higher value now carries the implication that the " primary oxide film " is discontinuous and heterogeneous.

(2) It has previously been shown (Vernon, *loc. cit.*) that each characteristic colour is associated with a definite weight-increment. In the case of the thinner coloured films produced at the lower temperatures (*e.g.*, the straw film at 225°) considerable evidence is now adduced that the " weight-increment film " (" secondary film "), if not entirely responsible for the colour, is structurally independent of the " primary film " beneath, from which it is readily separated by stripping. In the light of available electron-diffraction evidence it is reasonable to conclude that this secondary film consists predominantly of ferric oxide. The present results indicate, however, that there is also associated with the film a certain amount of metallic iron, the estimated contribution of which, in terms of thickness, is shown in Table XV (i).

TABLE XV.

Estimation of Film Thickness (*Means of Values for Pure Iron and Mild Steel*).

	(i) " Straw " film.			(ii) " Blue " film.		
	μg./cm.^{2}.	Calc. on apparent area of specimen, A.	Calc. on estimated " real " area, A.	μg./cm.^{2}.	Calc. on apparent area of specimen, A.	Calc. on estimated " real " area, A.
Secondary Fe_2O_3	10·2	190	76	22·3	425	170
Secondary Fe	1·3	17	7	2·1	25	10
Total secondary	—	207	83	—	450	180
Primary Fe_2O_3	5·0	95	38	5·0	95	38
Primary Fe	3·5	45	18	3·5	45	18
Total primary	—	140	56	—	140	56
Min. total thickness ...	—	290	120	—	520	210
Max. total thickness ...	—	350	140	—	590	240

Although the underlying primary oxide is structurally independent, the authors believe, with Miley (*loc. cit.*), that it contributes to the colour brought about by the presence of the overlying film. It seems unlikely, on general grounds, that refraction of incident light will be confined entirely to the outer film; further penetration into the altered iron surface beneath is to be expected, reflection finally taking place at the surface of unchanged metal. A further reason for bracketing the primary with the secondary film in assessing the total thickness of material responsible for the colour follows the discussion of the blue film (below). Combining the maximum and minimum values (with or without associated iron) for the primary and secondary films, we obtain maximum and minimum values of 350 A. and 290 A. (calculated on apparent area of specimen) for the " complete " straw film.

In the case of the thicker films at the higher temperatures (*e.g.*, the blue film at 275°), interpenetration of the primary and secondary components is indicated by the complete removal of both, on stripping, as a single film. For convenience, however, the two components are reckoned separately [Table XV (ii)] in computing film thickness. As before, a certain proportion of metallic iron is included as a possible component, the justification for which is based on the excess of total over ferric iron found in the film analysis. This procedure rejects the alternative interpretation (p. 626) that the excess iron represents ferrous oxide in the film, for which there appears to be no supporting evidence. On the other hand, the interpretation of excess metallic iron is in harmony with the views of Wagner (*Z. physikal. Chem.*, 1933, *B*, **21**, 25; see also Price, *Chem. and Ind.*, 1937, **56**, 769; Hoar and Price, *Trans. Faraday Soc.*, 1938, **34**, 867), according to which iron ions may diffuse outwards through the film under a potential gradient. Supporting experimental evidence had been previously supplied by Pfeil (*J. Iron Steel Inst.*, 1929, **119**, 501) for the oxidation of iron at much higher temperatures; it is also suggested by the recent work of Nelson (*loc. cit.*) and by the results described on p. 628. Of the alternative film thicknesses reported in Table XV, the authors attach greater weight to the " maximum " values, since the evidence appears to justify the view that metallic iron is associated with the ferric oxide in both the primary and the secondary films. The values of 350 A. and 590 A. (calculated on the apparent area of the specimen) obtained for the straw and for the blue films may be compared with the corresponding values of 460 A. and 720 A. derived optically by Constable. The divergences may be readily explained on the basis of the invalidity of the assumptions referred to on p. 622. Thus, it has been shown above that the film responsible for the characteristic colours cannot, as a whole, have the composition of massive ferric oxide; neither, or at least extremely improbably, can the lower reflecting " surface " correspond with a sharply defined interface between stoicheiometric ferric oxide and metallic iron; much more probably there is a gradual transition between metal and oxide. The most important single factor, however, is refractive index. Constable (*loc. cit.*), in calculating thicknesses from his carefully derived photometric data, employed Kundt's values (*Ann. Physik*, 1888, **34**, 484) for blue and red light (1·85 for blue film and 2·3 for straw film), although Kundt gave no details of the preparation of his oxides except to state that they were obtained by heating an iron prism in air. Tronstad and Höverstad (*Z. physikal. Chem.*, 1934, *A*, **170**, 172) give 3·5 as the refractive index of the " natural " oxide film on iron, and other values in the literature are 3·22 (Lange, " Handbook of Chemistry," 2nd edtn., 1937), 2·74 at $\lambda = 7000$ A. (Sosman and Hostetter, *J. Amer. Chem. Soc.*, 1916, **38**, 807), and for hæmatite from 2·7 to 3·2 (Mellor, " Comprehensive Treatise, etc.," Vol. XIII, 796, 797). Since magnetite has refractive index 2·42 ($\lambda = 7000$ A.) (Sosman and Hostetter, *loc. cit.*), it seems probable that Kundt's values were obtained on that oxide. If values of 3·03 (straw film) and 2·26 (blue film) are substituted for Kundt's values in Constable's calculations, then the optical values for thickness agree with the estimates of the present authors, *i.e.*, 350 A. for the straw, and 590 A. for the blue film. This agreement, and particularly the identity of the *ratios* for the two thicknesses as obtained by the present and by the optical method, confirms the validity of the assumption (see above) that the " straw film " (*i.e.*, the total thickness of material responsible for the straw colour) incorporates the " primary film," notwithstanding that the latter cleaves to the metal when the over-lying surface film is detached in the stripping process.

The results reported in Tables XI and XII, in which it was shown that the characteristic colours are produced at the appropriate temperatures and times even on the outside of an augmented primary film greatly exceeding in thickness that of the colour film itself, are not fully understood. It is clear, however, that the mechanism must involve (i) the transport of iron ions through the massive primary film with the production of a film of normal dimensions outside, (ii) the incorporation into this latter film of a fraction of the "augmented" primary film approximately equal in magnitude to the amount of the normal primary film on freshly-abraded specimens. This confirms that the colour of films produced on heating iron in air at temperatures above 200° is dictated primarily by the thickness of the film measurable by weight-increment (Vernon, *loc. cit.*); a certain amount of underlying oxidised material is utilised optically, but provided that this exceeds a very small minimum, its precise dimensions appear to be immaterial.

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APPENDIX.

Sloman's Vacuum-fusion Method.—Details of the vacuum-fusion technique, of which this note gives only the briefest outline, have been published by Sloman (*loc. cit.*). For the determination of total oxygen in massive iron or steel, cylindrical specimens (1—3 cm. long, 1 cm. in diam.) are used. After suitable preparation they are introduced into a side tube of the apparatus (which is then evacuated) preparatory to transference, electromagnetically, into a graphite crucible in which they are melted by high-frequency induction (temperature 1550°, pressure immediately before fusion 5×10^{-6} mm. of mercury). Oxygen contained in the sample is converted completely into carbon monoxide, the evolved gas, which is continuously pumped away, being collected in a suitable burette and examined in a gas-analysis apparatus of the Ambler type. The results obtained with a wide range of materials have yielded a high order of reproducibility.

The experiments that Mr. Sloman has carried out for the present work have involved the determination of the increase in total oxygen content of specimens, the oxidation of which is confined to an excessively thin layer of the surface. For this purpose it was necessary (i) that the material employed should have a uniform and preferably low initial content of oxygen, and (ii) that the surface area should be very large compared with the volume of the specimen. The high-purity iron (O, 0·0003; C, 0·017; S, 0·001; P, 0·001; Al, 0·004; Ni, 0·022%; Mn, trace; Cu, trace) prepared by Mr. C. A. Bristow in the Metallurgy Department of the National Physical Laboratory, besides meeting the first requirement, also enabled the second to be satisfied by reason of its high ductility. Sections measuring $1\frac{1}{4}'' \times 1\frac{1}{8}'' \times \frac{1}{4}''$ were cut from a bar of the massive metal and rolled, without any annealing heat-treatment, into strip having a thickness of 0·08—0·1 mm. (width 2·5—3·0 cm.); less pure material would have required intervening heat-treatments in which oxidation, sufficient to vitiate the experiments, would have been difficult, if not impossible, to avoid. By employing suitably small reductions during the cold-rolling (for which carefully cleaned jeweller's rolls were used), the temperature did not rise by more than a few degrees; the strip, moreover, was kept covered with high-grade vacuum-pump oil, so that low-temperature oxidation during rolling [see (*a*), below] was also severely restricted. For each vacuum-fusion experiment, three 20-cm. lengths of strip after heat-oxidation (six lengths in the case of invisible films formed at ordinary temperature) were each loosely coiled into a cylindrical spiral, 1 cm. in diam. (length 2·5—3·0 cm.). The total surface area so obtained was 500—1000 sq. cm. (weight of strips 20—40 g.) as compared with 12 sq. cm. for the usual massive specimen weighing *ca.* 18 g.

The experiments were carried out on the following: (*a*) Strips rolled and degreased but not abraded, for determination of oxygen introduced during rolling. (*b*) Strips abraded with Hubert No. 1 emery paper [following treatment (*a*)] and subsequently degreased, for determination of oxygen taken up during abrasion (For reasons explained in the text, a period of about an hour was allowed to elapse between abrasion and vacuum fusion, the specimen, meanwhile, being kept in a desiccator in presence of air.) (*c*) Strips heated in air at appropriate temperature (abrasion and degreasing as above), for determination of oxygen taken up during the standard heat-treatment described in the text. These strips were weighed before and after exposure.

The results obtained may be summarised as follows:

(*a*) Oxygen in massive metal, per 100 g. = $\left.\begin{array}{l}\text{(i) } 0{\cdot}0003_7 \\ \text{(ii) } 0{\cdot}0003_1\end{array}\right\}$ Mean $0{\cdot}0003_4$ g.
Oxygen in rolled strip, per 100 g. = 0·0017 g.
Oxygen added during rolling = 0·0014 g. per 100 g. = 0·56 µg./cm.^{2}.
(Surface area of rolled strip = 2460 cm.^{2} per 100 g.)

The oxide corresponding to this small amount of surface oxygen is probably entirely removed in the subsequent abrasion; this assumption is necessary if the subsequent value (approximately 3 times greater) is accepted as corresponding exactly to the amount of oxide forced into the surface in the act of abrasion.

(*b*)

O_2 in massive metal, per 100 g.	O_2 in rolled abraded strip, per 100 g.	Surface area of rolled strip, cm.^{2} per 100 g.	O_2 added by (rolling and) abrasion: per 100 g.	µg./cm.^{2}.	
(i) $0{\cdot}0003_4$ (mean)	0·0042	2459	0·0039	1·57	Mean 1·52
(ii) $0{\cdot}0003_4$ („)	0·0040	2493	0·0037	1·48	
(iii) 0·0014	0·0049	2312	0·0035	1·51	

Experiments (i) and (ii) were carried out with the N.P.L. "pure iron"; for experiment (iii) carbonyl iron (a high-purity iron supplied by I.G. Farbenindustrie A.G.) was employed.

It is clear that the figure of 1·5 µg./cm.^{2} may be safely accepted as representing the total increase in surface oxygen resulting from the standard method of abrasion.

(*c*) Results of heat-oxidation experiments were obtained from both carbonyl iron and N.P.L. iron, as follows:

Iron.	Temp. and time of heating.	O_2 in massive metal before heating, per 100 g.	O_2 in strip after heating, per 100 g.	Surface area of rolled strip, cm.^{2}/100 g.	Increase in surface oxygen due to heating (µg./cm.^{2}). By vacuum fusion.	By weighing.
N.P.L.	275° (75 mins.)	$0{\cdot}0003_4$	(i) 0·0250	2413	8·69	8·69
			(ii) 0·0247	2361	8·81	8·80
Carbonyl	225° (150 mins.)	0·0014	0·0110	2312	2·64	2·72

These data (see also Sloman, Iron and Steel Inst., Eighth Report on Heterogeneity of Steel Ingots, Second Oxygen Sub-committee Report, 1939) illustrate the accuracy and reproducibility of the vacuum-fusion results, the significance of which in relation to the present inquiry is discussed in the text.